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SERS spectra of $(NH_3)_2(CH_2)_2HXO_4$ (X = P, As) adsorbed in silver colloids

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Abstract : SERS spectra of $(NH_3)_2(CH_2)_2HPO_4$ and $(NH_3)_2(CH_2)_2HAsO_4$ are recorded in two types of silver colloids. In the phosphate, two distinct adsorption sites are present which give rise to different enhanced bands in the two colloids. The ethylene diammonium group is close to the silver surface in one colloid whereas the phosphate group is closer in the second colloid. In the arsenate, bands due to both ethylene diammonium and arsenate groups are enhanced in one type of colloid whereas in the second colloid only the bands due to the arsenate ions are enhanced.

Keywords : SERS spectra, silver colloid, adsorption sites, ethylene diammonium phosphate, ethylene diammonium arsenate

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Surface Enhanced Raman Scattering (SERS) spectroscopy is a powerful tool for investigating the co-ordination and geometry of adsorbed molecules on metal surfaces. Phosphates being poor scatterers are expected to be good adsorbers compared to arsenates [1]. In continuation of our earlier study [2] on the IR and polarized Raman spectra of $(NH_3)_2(CH_2)_2HPO_4$, ethylene diammonium phosphate (EDP), and $(NH_3)_2(CH_2)_2HAsO_4$, ethylene diammonium arsenate (EDA), we report here the results of their SERS spectra in silver colloids. Greaves and Griffith [1] have investigated the SERS spectra of certain vanadates, phosphates and arsenates and found larger enhancement factor for phosphate compared to arsenates. They also noticed that larger anions interact less effectively with the silver surface.

Two different silver colloids (i) greenish-yellow (colloid 1) and (ii) greenish-grey (colloid 2) have been used in the investigation. Colloid 1 prepared [3] from sodium

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borohydride and silver nitrate has a strong absorption maximum at 390 nm. Colloid 2 is prepared [4] using silver nitrate and sodium citrate and has a broad absorption band around 430 nm. For recording SERS spectra, the samples are prepared by mixing equal volumes of colloid 1/ colloid 2 and 10^{-4} M aqueous solution of the compound. Normal Raman spectra could not be obtained for aqueous solutions of the compounds. SERS spectra of the compounds in freshly prepared colloid 1 are also recorded. The chemicals have been procured from Sigma, USA and deionized water has been used throughout. Raman spectra were recorded on a Dilor GMBH Z 24 spectrometer using 514.5 nm radiation (power 200 mW) of an Ar^+ laser. Absorption spectra were recorded using a UV-Shimadzu UV-Visible recording spectrophotometer.

EDP and EDA have absorption bands around 340 and 400 nm respectively. The addition of 10^{-4} M aqueous solution of EDP to colloid 1 changes the colour of the solution to light pink with an additional very broad absorption band around 620 nm. However in colloid 2, the absorption band around 430 nm becomes broadened with another extinction maximum around 700 nm. EDA in colloid 1 shows two broad bands around 650 and 395 nm. As in EDP in colloid 2, the band around 430 nm becomes more broadened.

In the SERS spectrum of EDP (Figure 1), a low frequency band is observed at 234 cm^{-1} in colloid 1 and at 217 cm^{-1} in colloid 2. Further, in colloid 1 bands corresponding to $(NH_3)_2(CH_2)_2^{2+}$ are enhanced which are not observed in colloid 2 (Table 1). The symmetric

Table 1. SERS spectral data (cm^{-1}) and band assignments

EDP in colloid 1	EDP in colloid 2	EDA in colloid 1	EDA in colloid 2	Assignment
1598 mbr		1627 m		δNH_3^+
1476 m				δCH_2
1387 mbr		1364 m		t CH_2, w CH_2
		1163 m		r NH_3^+
	1053 mbr			ν_{as} $PO_3(E)$
	952 s			ν_s $PO_3(A_1)$
		812 vs	810 m	ν_s AsO_4^{3-}
675 m				Combination
	595 sh			δ_{as} $PO_3(E)$
	545 sh			δ_s $PO_3(A_1)$
468 s	444 s	470 s	472 vs	δC–CN
440 s			455 vs	δAsO_4^{3-}
234 s		221 m		νAg–N
	217 m			νAg–O

v–very, s–strong, m–medium, br–broad, sh–shoulder, t–twisting, w–wagging, r–rocking

and asymmetric stretching and bending modes of PO_3 are not observed in colloid 1. However, these are observed at 952, 1053, 545 and 595 cm^{-1} in colloid 2. These

observations suggest that the $(NH_3)_2(CH_2)_2^{2+}$ and HPO_4^{2-} groups are close to the silver surface in colloid 1 and colloid 2 respectively. In otherwords, there are two adsorption sites in EDP which is supported by the low frequency bands at 234 and 214 cm^{-1} in colloid 1 and colloid 2 respectively. Bands in the SERS spectrum recorded in freshly prepared colloid 1 (Figure 1) are not intense. It seems that aged colloid is a better substrate for surface enhancement.

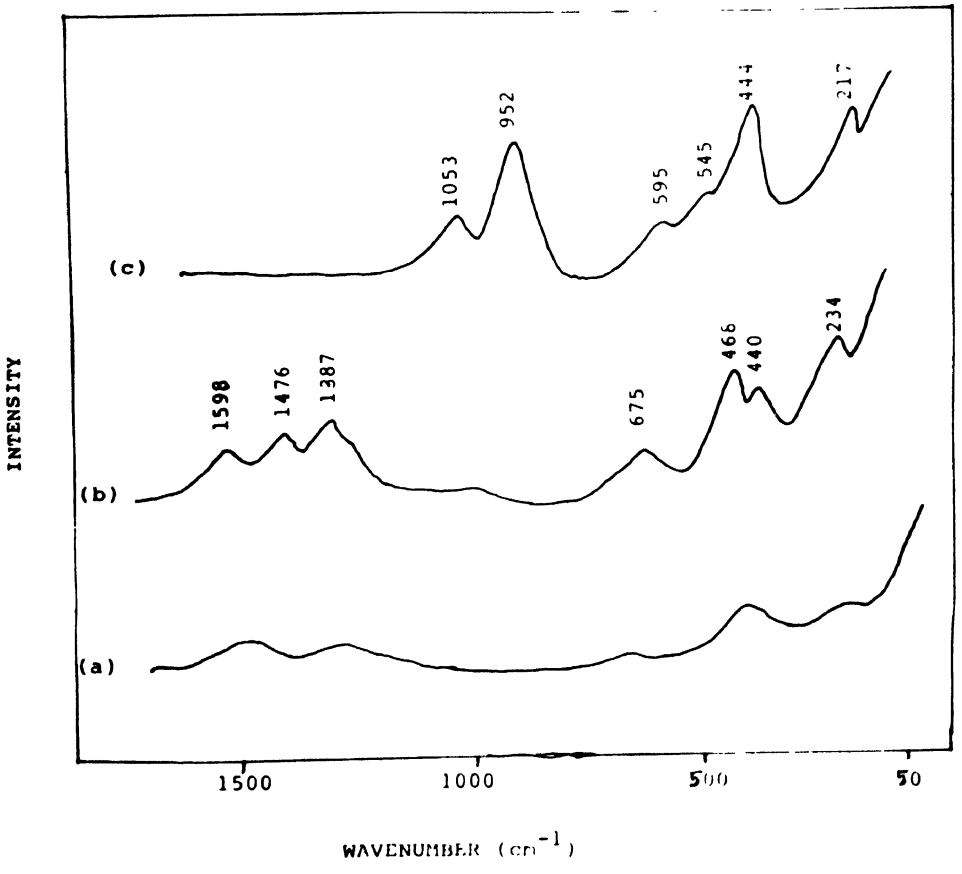

Figure 1. SERS spectrum of EDP
(a) in fresh colloid 1
(b) in aged colloid 1
(c) in colloid 2.

In the case of EDA, bands due to both ethylene diammonium and arsenate groups are enhanced in colloid 1. In addition, a low frequency band at 221 cm^{-1} is observed (Figure 2). No splitting is observed for the stretching and bending modes of the arsenate ion indicating a higher symmetry for the ion when compared with the phosphate. In otherwords, the symmetry of the ion is probably not lowered due to adsorption or the ion may be existing as AsO_4^{3-} rather than $HAsO_4^{2-}$. In colloid 2, only bands due to the arsenate ion are enhanced

(Figure 2 and Table 1). Though the arsenate bands are enhanced in both the colloids, low frequency band which corresponds to silver-molecule stretching mode is observed only in colloid 1. Therefore, it is reasonable to assume that the band observed at 221 cm^{-1} is due to ν Ag–N mode arising from the nearness of the ethylene diammonium group to the silver surface. The non-observation of the low frequency ν Ag–O band in both the colloids suggests that the enhancement of the arsenate bands is probably due to the electromagnetic field contribution.

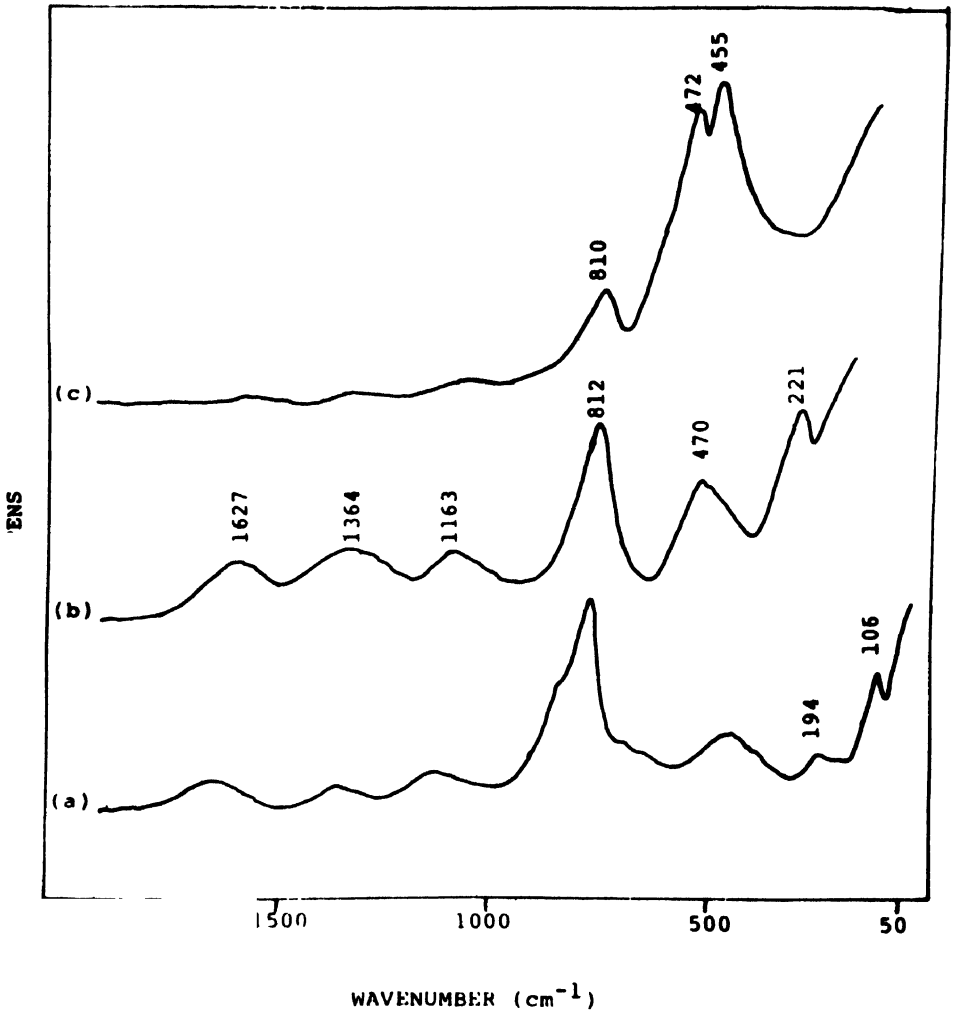

Figure 2. SERS spectrum of EDA
(a) in fresh colloid 1
(b) in aged colloid 1
(c) in colloid 2.

SERS spectrum recorded in fresh colloid 1 (Figure 2) showed two low frequency bands at 194 and 106 cm^{-1}. Further, only the arsenate bands are prominent in the spectrum.

As the colloid is aged only a medium intense band around 221 cm^{-1} is observed for this low frequency Ag-molecule stretching mode and both ethylene diammonium and arsenate bands are enhanced.

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